

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-160623

(43)Date of publication of application : 21.06.1996

(51)Int.Cl. G03F 7/039
 G03F 7/004
 G03F 7/004
 G03F 7/029
 G03F 7/075
 H01L 21/027

(21)Application number : 06-331724

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(22)Date of filing : 09.12.1994

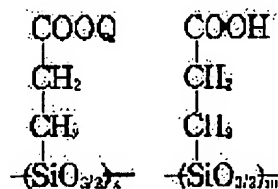
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(54) POSITIVE TYPE RESIST MATERIAL

(57)Abstract:

PURPOSE: To provide a positive type resist material sensitive to high-energy beams, excellent in sensitivity and resolution, useful for the fine machining by electron beams or far ultraviolet rays, having little absorption at the exposure wavelength of the KrF excimer laser in particular, capable of easily forming a fine pattern perpendicular to a board, excellent in oxygen plasma etching resistance, and capable of forming a fine pattern at a high aspect ratio when this resist film is applied on a lower-layer resist to form a two-layer resist.

CONSTITUTION: This positive type resist material can be developed in an alkali aqueous solution containing two components of a silicone polymer expressed by the



formula and an acid generating agent decomposed by the action of the illuminated radioactive rays to generate acid. In the formula, Q indicates the t-butyl group, t-butoxy carbonyl methyl group, trimethyl silyl group, or tetrahydropyranyl group, $x+m=1$, and (x) is non-zero.

LEGAL STATUS

[Date of request for examination] 23.04.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3175514

[Date of registration] 06.04.2001

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

[Formula 1]



(Q shows t-butyl, a t-butoxy carbonylmethyl radical, a trimethylsilyl radical, or a tetrahydropyranyl group among a formula.) x is not set to 0 although the integer of 1-3, x, and m of n are $x+m=1$. Positive-resist ingredient in which development with the alkali water solution containing two components of the silicone polymer shown and the acid generator which decomposes according to an operation of the radiation irradiated and generates an acid is possible.

[Claim 2] An acid generator is the following general formula (2).

(R) pJM -- (2)

(R shows an aromatic series radical or a permutation aromatic series radical the same or of a different kind among a formula, J shows sulfonium or iodonium, and M shows a toluene sulfonate radical or a trifluoromethane sulfonate radical.) p is 2 or 3. Ingredient according to claim 1 which is onium salt shown.

[Claim 3] Furthermore, the ingredient according to claim 1 or 2 which added the lysis inhibition agent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention has high sensibility to high energy lines, such as far ultraviolet rays, an electron ray, and an X-ray, and relates to the positive-resist ingredient

suitable for ultra-fine processing technology which can form a pattern by developing negatives in an alkali water solution.

[0002]

[Description of the Prior Art] the resist ingredient which performs chemistry magnification (chemical amplification) by making into a catalyst the acid developed in recent years with high integration and high-speed-izing of LSI -- [-- for example Journals, such as Lew (Liu) OBU Vacuum Science And technology (J. Vac.Sci.Technol.), the Bth -- six volumes and 379th page (1988)] have the conventional high sensitivity resist ingredient and the sensibility more than an EQC, and moreover, its definition is high and they have the outstanding description also with high dry etching resistance. Therefore, it is a resist ingredient especially promising for far-ultraviolet-rays lithography. However, although Shipley (Shipley) has already commercialized 3 component chemistry magnification resist ingredient (trade name SAL601ER7) which consists of novolak resin, a melamine compound, and an acid generator as a negative-resist ingredient, there is nothing that was still commercialized as a positive-resist ingredient of a chemistry multiplier system. Therefore, on the production process of LSI, although wiring, gate formation, etc. could respond with the negative-resist ingredient, since processing detailed to a fogging and cone sake was difficult, by contact hole formation having used the negative-resist ingredient, the highly efficient positive-resist ingredient was demanded strongly.

Conventionally, Ito (Ito) etc. adds onium salt to resin called PBOCST which protected the OH radical of polyhydroxy styrene by the t-butoxycarbonyl group (t-BOC radical), and is developing the chemistry magnification resist ingredient of a positive type.

[0003] However, the viewpoint of the pollution control to a substrate to [bibliography:Pori Mars Inn electronics, the 242nd time (Polymers in Electronics, ACS symposium Series) (American Chemical Society, Washington DC.1984) of ACS symposium series, the 11th page], and the PBOCST resist ingredient of the used onium salt are not desirable as a metal component on a process excluding antimony.

[0004] on the other hand, Ueno etc. announces the far-ultraviolet-rays chemistry magnification mold positive-resist ingredient which has the high sensitivity and high definition which used Pori (p-styrene oxy-tetrahydropyranyl) as the principal component -- **** (reference: the 36th Japan Society of Applied Physics related union lecture meeting, 1989, 1 p-k -7) -- it was difficult from the mechanical strength of a pattern to form the detailed pattern of a high aspect ratio with high precision.

[0005] Moreover, although many chemistry multiplier system positive-resist ingredients which have sensibility in this way to the far ultraviolet rays, electron ray, and X-ray which used novolak resin and polyhydroxy styrene as base resin are announced conventionally, it is difficult for the present condition for all to be monolayer resists, to still have the problem of a substrate level difference, the problem of the standing wave by the light reflex from a

substrate, and a problem with the difficult pattern formation of a high aspect ratio, and to present practical use.

[0006] By the way, the two-layer resist method is excellent on the level difference substrate carrying out pattern formation of a high aspect ratio. In order to carry out alkali development by the two-layer resist method, the silicone system polymer which has hydrophilic radicals, such as a hydroxy group and a carboxyl group, was needed, but since the silanol to which the direct hydroxy group was attached to this silicone produced crosslinking reaction with an acid, application into a chemistry magnification mold positive-resist ingredient was difficult.

Moreover, there is polyhydroxy benzyl silsesquioxane as a stable alkali solubility silicone polymer, and it is known that the ingredient which protected a part of the hydroxy group by t-BOC will turn into a silicone system positive-resist ingredient of a chemistry magnification mold in combination with an acid generator (JP,6-118651,A or SPIE Vol.1925 (1993) 377). however, the polymer used for these silicone resist ingredients -- a phenyl group -- having -- **** -- not a little -- ** -- since it has absorption in ultraviolet rays, the permeability of the resist film becomes low. So, it is difficult to attain high resolution in a high sensitivity-ized list to far-ultraviolet-rays exposure.

[0007] In order to make it dissolve the exposure section in a developer, many protective groups must be made to decompose, since all hydrophilic groups, such as a carboxyl group required [although the thing of JP,5-323611,A is mentioned as an example] in order that this base polymer may enable alkali development, and a hydroxy group, are protected, although it does not have the phenyl group in the base polymer of a silicone positive-resist ingredient. Therefore, the addition of the acid generator to add increases or sensibility worsens.

Furthermore, possibility of causing change of the thickness produced when many protective groups are made decomposing in addition, and the stress in the film or generating of air bubbles is high, and high sensitivity and the resist suitable for detailed processing are not given.

[0008] This invention was made in view of the above-mentioned situation, and is suitable as a two-layer resist ingredient, and it aims at offering the chemistry magnification mold silicone system positive-resist ingredient excellent in high sensitivity, high definition, and process applicability.

[0009]

[Means for Solving the Problem and its Function] this invention person did the knowledge of the effective thing from the point that using the silicone polymer shown by the following general formula (1) as a silicone polymer obtains high-sensitivity-izing and high resolution, as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose.

[0010]

[Formula 2]



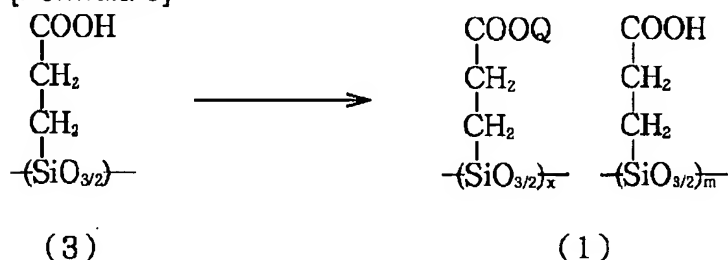
(Q shows t-butyl, a t-butoxy carbonylmethyl radical, a trimethylsilyl radical, or a tetrahydropyranyl group among a formula.) x is not set to 0 although the integer of 1-3, x, and m of n are $x+m=1$.

[0011] That is, this invention persons were except the silicone polymer with a phenyl group which is in JP,6-118651,A, they gave high permeability to the light of a far-ultraviolet field, did not protect all the alkali fusibility radicals by the acid unstable radical, but protected partially, and examined and searched high sensitivity for the polymer which gives high resolution wholeheartedly. A silicone polymer as which an addition reaction produces that the silicone polymer which does not have a phenyl group, on the other hand, makes a polysiloxane with a hydrogen atom carry out the high DOROSHI relation reaction of unsaturated carboxylic acid like a methacrylic acid like the synthetic approach of being here although a silicone polymer with an ethyl carboxy group which is in JP,5-323611,A is mentioned in the alpha position of unsaturated carboxylic acid, and is illustrated chiefly is difficult to get. Moreover, it is quantitatively difficult to perform a high DOROSHI relation reaction into a polymer, and it becomes difficult to supply a silicone polymer to stability, and quality control of a resist becomes difficult further.

[0012] As a result of examining many things, this invention persons industrially available 2-cyano ethyl trichlorosilane then, by adding and hydrolyzing to underwater easily Under the hydrochloric acid which it not only obtains a desired polysiloxane frame, but the cyano group produced in coincidence at the time of hydrolysis of trichlorosilane, It can find out hydrolyzing to a carboxylic acid and the Pori (2-hydroxy carbonylethyl) siloxane of the following type (3) can be obtained easily. Furthermore, by protecting the carboxylic acid of this formula (3) by t-butyl, the t-butoxy carbonylmethyl radical, the trimethylsilyl radical, or the tetrahydropyranyl group partially The silicone polymer shown by the following general formula (1) finds out excelling in the base resin which obtains high resolution by high sensitivity.

[0013]

[Formula 3]



(Q and mx have the semantics as above-mentioned among a formula.)

[0014] Therefore, this invention offers the positive-resist ingredient in which development is possible in the alkali water solution of the silicone polymer shown by the above-mentioned general formula (1), and the acid generator which decomposes according to an operation of the radiation irradiated and generates an acid which contains a lysis inhibition agent as occasion demands two components further.

[0015] Hereafter, when it explains in detail, per this invention and also the polymer used for the positive-resist ingredient of this invention are silicone polymers shown by the following general formula (1).

[0016]

[Formula 4]



[0017] Here, Q shows t-butyl, a t-butoxy carbonylmethyl radical, a trimethylsilyl radical, or a tetrahydropyranyl group. n shows the integer of 1-3. Moreover, although x and m are $x+m=1$, it is the positive number of $x > 0$, and m is the positive number of $0 < m < 1$. However, when x in a formula is small, since the dissolution inhibition effectiveness is small, it becomes indispensable to add an inhibitor. Since the alkali solubility of a polymer will fall if x becomes large, an inhibitor becomes unnecessary. As for x, 0.05-0.5 are desirable. Less than 0.05, if the dissolution inhibition effectiveness is small and larger than 0.5, oxygen plasma-etching resistance may fall with a silicone-content fall. And since the solubility to an alkali water solution will fall to the degree of pole if larger than 0.5, sensibility may fall to the degree of pole in the developer currently generally used.

[0018] Moreover, as for the weight average molecular weight of the silicone polymer used by this invention, 5,000-50,000 are desirable. When smaller than 5,000, the problem by which desired plasma resistance is not acquired that the lysis inhibition effectiveness over an alkali water solution is low arises, and when higher than 50,000, the problem which stops being able to melt into a general-purpose resist solvent easily may arise.

[0019] In addition, the silicone of a formula (1) can be obtained by protecting the carboxyl group, after hydrolyzing and condensing 2-cyano ethyl trichlorosilane and obtaining the Pori (2-hydroxy carbonylethyl) siloxane of a formula (3), as mentioned above.

[0020] Here, the approach of protecting the carboxylic acid in a polymer by t-butyl is easily attained by making it react with butyl alcohol under anhydrous trifluoromethane acetic-acid existence.

[0021] Moreover, the protection by the t-butoxy carboxymethyl radical of a carboxylic acid can perform bromoacetic acid t-butyl easily by reacting under base existence.

[0022] A reaction with trimethylsilyl chloride can perform almost quantitatively the approach of protecting a carboxylic acid by the trimethylsilyl radical under base existence like triethylamine and a pyridine.

[0023] The approach of tetrahydropyranyl-izing a carboxylic acid can be easily performed at a reaction with a dihydropyran under weak acid existence.

[0024] especially 80% or more of the loadings of the silicone polymer used for this invention are desirable more than 55% (% of the weight and the following -- the same) to the total loadings which both 3 component system and two-component system combined with other components. At less than 55%, the spreading nature of a resist ingredient may have bad loadings, or the reinforcement of the resist film may be bad.

[0025] In this invention, although the acid generator which decomposes to high energy lines irradiated, such as far ultraviolet rays, an electron ray, and an X-ray, and generates an acid is blended, oxime sulfonic-acid derivative, 2, 6-dinitro benzyl sulfonic-acid derivative, naphthoquinone-4-sulfonic-acid derivative, 2, 4-Bisto RIKURORO methyl-6-aryl-1,3,5-triazine derivative, alpha, and alpha'-screw aryl sulfonyl diazomethane etc. is mentioned as this acid generator. However, these acid generators may be unable to obtain a high sensitivity resist ingredient, and, for this reason, are the following general formulas (2).

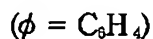
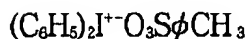
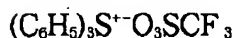
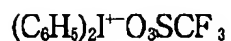
(R) pJM -- (2)

(R shows an aromatic series radical or a permutation aromatic series radical the same or of a different kind among a formula, J shows sulfonium or iodonium, and M shows a toluene sulfonate radical or a trifluoromethane sulfonate radical.) p is 2 or 3. The onium salt shown is used preferably.

[0026] The compound shown by the following formula as an example of this onium salt is mentioned, and these can be used.

[0027]

[Formula 5]



[0028] However, any of these acid generators may be difficult for solubility to be low and to mix optimum dose in a resist ingredient to the general-purpose and suitable solvent for spreading of resist ingredients, such as ethylcellosolve acetate, ethyl lactate, and ethoxy-2-propanol, for this reason. Moreover, there is also a thing with the fault which a sensibility change with time and change of a pattern configuration will tend to produce by the time it performs heat treatment after that it is difficult to form the good resist film and an optical exposure since compatibility with a silicone polymer is bad even if the solubility over a solvent is high. When especially compatibility is a bad acid generator, distribution in the resist film is produced and an overhang may be observed in a pattern front face. In a chemistry magnification resist ingredient, or an acid deactivates in a resist film front face, when an acid generator is lost on a front face, such a phenomenon is produced well.

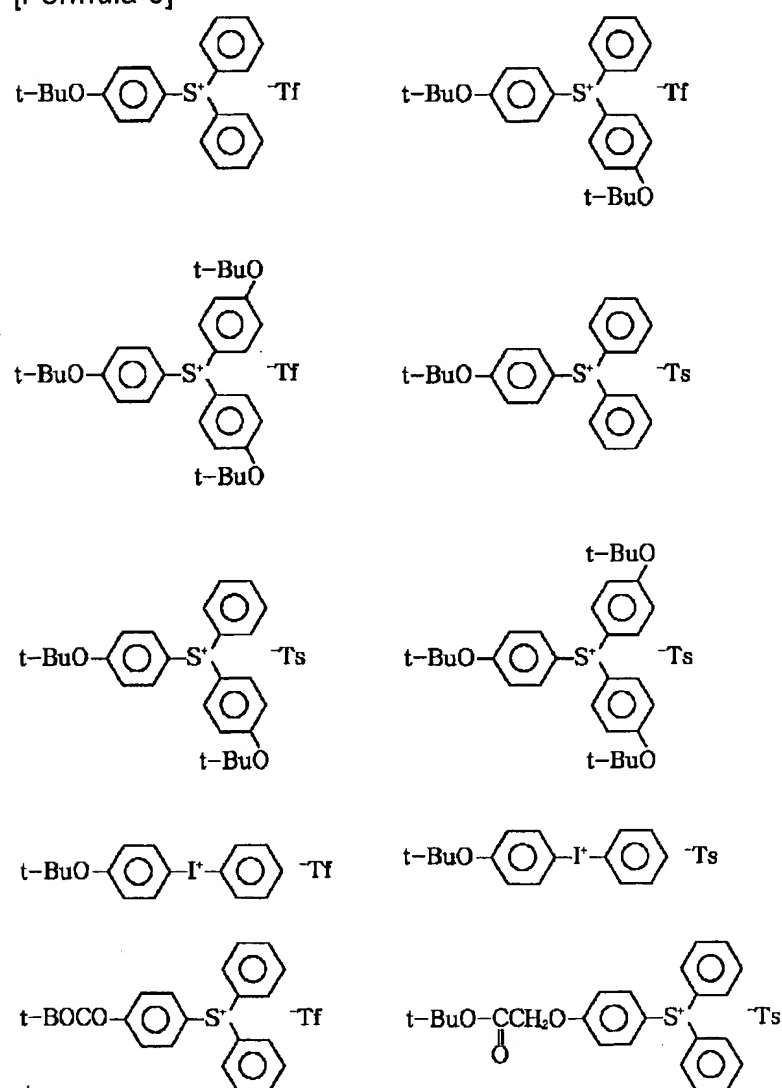
[0029] Therefore, the onium salt of the phenyl group permuted as onium salt of the acid generator used still more preferably by t-alkoxy group at least one of the R of the above-mentioned general formula (2) is indicated to be by R13CO- (R1 is a permutation or unsubstituted monovalence hydrocarbon groups, such as an alkyl group of carbon numbers 1-10 and an aryl group), t-butoxycarbonyloxy radical, or the t-butoxy cull BONIRUMETOKISHI radical is used preferably. It is the features that dissolve in a general-purpose resist solvent easily, and the solubility compatibility with a silicone polymer being not only good but after exposure is excellent, and a pattern can form these onium salt perpendicularly to a substrate. Since at least one of the R of a general formula (2) is a t-alkoxy phenyl group, t-butoxycarbonyloxy phenyl group, or a t-butoxy cull BONIRUMETOKISHI phenyl group at this time and a phenolic hydroxyl group or a carboxylic acid is produced at the time of exposure and heat treatment, the solubility after exposure is improved. Although onium salt generally

shows the dissolution inhibition effectiveness, these onium salt has a dissolution facilitatory effect after exposure. For this reason, since the dissolution rate difference before and behind exposure can be enlarged, it is used preferably. It is in the inclination for solubility to be excellent, so that there is many R permuted by t-alkoxy group, t-butoxycarbonyloxy radical, or the t-butoxy cull BONIRUMETOKISHI radical.

[0030] The compound in which the example of the onium salt by which at least one of the R of the above-mentioned general formula (2) was permuted by t-alkoxy group, t-butoxycarbonyloxy radical, or the t-butoxy cull BONIRUMETOKISHI radical is shown by the following formula is mentioned.

[0031]

[Formula 6]



(Tf shows p-trifluoromethane sulfonate among a formula, Ts shows p-toluene sulfonate, and t-BOC shows a t-butoxycarbonyl group.)

[0032] 1 - 10% of especially the content of the above-mentioned acid generator is suitable 0.5

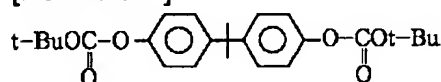
to 15%. Sensibility is low although the resist property of a positive type is shown at least less than 0.5%. Although resist sensibility shows the high-sensitivity-ized inclination, and the resist property of a positive type is shown even if [than 15%] more [contrast (gamma) improves and] when the content of an acid generator increases That the further high sensitivity-ization by the increment in a content is not expectable, that onium salt is an expensive reagent, that the increment in the low-molecular component in a resist reduces the mechanical strength of the resist film, when oxygen plasma resistance also falls, 15% or less of the content of onium salt is suitable.

[0033] The resist ingredient of this invention can be used also as a 3 component system resist ingredient which it not only can use it as a two-component system resist ingredient which consists of a silicone polymer shown by the general formula (1), and an acid generator, but added the lysis inhibition agent if needed.

[0034] What t-BOC-ized the ingredient which t-BOC-ized the OH radical <TXF FR=0002 HE=025 WI=080 LX=1100 LY=1700> of bisphenol A which can use the thing same as such a lysis inhibition agent as well-known 3 component system resist ingredient, for example, is shown by the following formula, phloroglucine, a tetra-hydroxy benzophenone, etc. can be used.

[0035]

[Formula 7]



[0036] 40% or less of the content of a lysis inhibition agent is good, and it is desirable to consider as 10 - 30% especially. If [than 40%] more, since the oxygen plasma resistance of the resist film falls remarkably, it becomes impossible to use it as a two-layer resist.

[0037] Although the resist ingredient of this invention can prepare a lysis inhibition agent if needed the above-mentioned silicone polymer, an acid generator, and by dissolving in an organic solvent further That to which these components are fully dissolved and the resist film spreads in homogeneity as an organic solvent is desirable. Specifically Butyl acetate, a xylene, an acetone, a cellosolve acetate, Ethylene glycol monomethyl ether, the diethylene-glycol monomethyl ether, Ethylene glycol monoethyl ether, diethylene-glycol dibutyl ether, diethylene-glycol wood ether, ethyl lactate, methyl lactate, lactic-acid propyl, butyl lactate, etc. can be mentioned. One of them may be independently used for these organic solvents, or it may be used for them combining two or more sorts. In addition, it is suitable for the loadings of this organic solvent to consider as the amount of several times of the total amount of the above-mentioned component.

[0038] In addition, the resist ingredient of this invention is not hindered by blending a surfactant etc. further.

[0039] As the pattern formation using the resist ingredient of this invention is the following, it can be performed. First, it prebakes by carrying out spin spreading of the resist solution of this invention on a substrate, and a high energy line is irradiated. Under the present circumstances, an acid generator decomposes and an acid is generated. By performing PEB (Post Exposure Bake), an acid unstable radical decomposes by making an acid into a catalyst, and the lysis inhibition effectiveness disappears. Subsequently, negatives can be developed in an alkali water solution and a positive type pattern can be formed by carrying out a rinse with water.

[0040] Moreover, by having used the silicone polymer as base resin, since this invention resist is excellent in oxygen plasma-etching resistance, it is useful also as a two-layer resist.

[0041] That is, spin spreading of the resist solution of this invention is carried out on it after forming an organic polymer layer thick as a lower layer resist on a substrate. Since a lower layer resist is alternatively etched by performing etching after performing pattern formation by the same approach as the above, the resist layer of upper this invention can form the upper resist pattern in a lower layer.

[0042] In a lower layer resist, after being able to use a novolak resin system positive resist and applying on a substrate, INTAMIKISHINGU with a silicone system resist can be prevented by carrying out postbake at 200 degrees C for 1 hour.

[0043]

[Effect of the Invention] Since the positive-resist ingredient of this invention induces a high energy line and is excellent in sensibility and definition, it is useful to micro processing by the electron ray or far ultraviolet rays. Especially, since absorption on the exposure wavelength of a KrF excimer laser is small, it has the description that it is detailed and a perpendicular pattern can moreover be easily formed to a substrate. Moreover, since it excels in oxygen plasma-etching resistance, the two-layer resist which applied the resist film of this invention on the lower layer resist also has the description that a detailed pattern can be formed by the high aspect ratio.

[0044]

[Example] Although a synthetic example and an example are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0045] [Synthetic example 1] Synthetic 2-cyano ethyl trichlorosilane 188.5g (1.0 mols) of the Pori (2-hydroxy carbonylethyl) siloxane was dissolved in toluene 200g, and dropping addition was carried out, agitating at a room temperature into 500g of water. Churning aging was performed at the reflux temperature of a reaction solution after dropping termination for 5 hours. After cooling, after separating the acid water layer, rinsing the organic layer by 1l. of water subsequently and a water layer's becoming neutrality from a reaction mixture, rinsing was performed twice [further]. Although colorless oily matter was obtained when the evaporator was used and the strip of the toluene was carried out after filtering by separating an

organic layer, this was crystallized underwater, filtration and desiccation were performed and the Pori (2-hydroxy carbonylethyl) siloxane was obtained with the yield of 102.5g (yield: 82%). [0046] In IR of the obtained polymer, there is no absorption peak of the $2,200\text{cm}^{-1}$ neighborhood peculiar to a cyano group, and it turned out that the cyano group is quantitatively changed into the carboxylic acid under that an absorption peak is seen by $1,650\text{cm}^{-1}$ [peculiar to a carboxylic acid], and the hydrochloric-acid acidity ambient atmosphere produced by having not detected an unreacted cyano group in ^{13}C -NMR at the time of hydrolysis of chlorosilicane.

[0047] Moreover, the weight average molecular weight of the obtained polymer was 6,250.

[0048] [Synthetic example 2] 60.7g (0.08 mols) of t-butyl alcohol was added gradually, having dissolved 62.5g and 125g (0.6 mols) of anhydrous trifluoroacetic acid of a polymer obtained in the example 1 of t-butyl-ized composition of the Pori (2-hydroxy carbonylethyl) siloxane in acetone 250ml, and agitating in a room temperature. After riping for 5 hours, the strip of the acetone of unreacted t-butyl alcohol and a reaction solvent was carried out. The obtained reaction mixture was added into 1l. of water, crystallization was performed, and precipitation of a polymer was obtained. Precipitation was rinsed twice [further] and the polymer which the Pori (2-hydroxy carbonylethyl) siloxane formed into t-butyl was obtained after filtration and desiccation.

[0049] In analysis by NMR of the obtained polymer, the rate of the formation of t-butyl was 21%.

[0050] [Synthetic example 3] 62.5g and pyridine 47.4g (6.0 mols) of a polymer obtained in the example 1 of t-butoxy carbonylmethyl-ized composition of the Pori (2-hydroxy carbonylethyl) siloxane were dissolved in dimethyl sulfoxide 250ml, and 15.2g (0.078 mols) of t-butyl bromoacetic acid was added, agitating in the reaction temperature of 80 degrees C. After riping at 80 degrees C for 8 hours, the reaction mixture was added in 5l. of water, and the white polymer was obtained. Filtration and desiccation were performed after rinsing this polymer twice. As a result of analyzing a polymer by NMR, it was the polymer which formed the carboxylic acid of the Pori (2-hydroxy carbonylethyl) siloxane into 13%t-butoxy carbonylmethyl.

[0051] [Synthetic example 4] Trimethylsilyl chloride 23.3g (0.156 mols) was added having dissolved in acetone 250ml and agitating under reflux 62.5g and pyridine 47.4g (6.0 mols) of a polymer obtained in the example 1 of trimethylsilylation composition of the Pori (2-hydroxy carbonylethyl) siloxane. Under reflux, after performing aging for 5 hours, the reaction mixture was added to 1l. water, and the white polymer was obtained. Filtration and desiccation were performed after repeating rinsing twice. When the obtained polymer was analyzed by NMR, it was the polymer which trimethylsilylated the carboxylic acid of the Pori (2-hydroxy carbonylethyl) siloxane 24%.

[0052] [Synthetic example 5] Dihydropyran 43.5g (0.5 mols) was added over 1 hour, having dissolved 62.5g and pyridinium tosylate 2.5g of a polymer obtained in the example 1 of tetrahydropyranyl-ized composition of the Pori (2-hydroxy carbonylethyl) siloxane in acetone 250ml, and agitating at a room temperature. After performing aging at a room temperature for 8 hours, the strip of the acetone of reaction mixture was carried out, and it dissolved in the methanol, added to 5l. water, and white precipitation was obtained. When the Pori (2-hydroxy carbonylethyl) siloxane tetrahydropyranyl-ized when rinsing of precipitation was repeated 5 times and filtration and desiccation were performed was obtained and having been analyzed by NMR, the rate of installation of a tetrahydropyranyl group was 17.4%.

[0053] [Example 1]

Base resin (synthetic example 2) 96 weight sections p-t-BUTOKISHIFENIRU diphenyl trifluoromethane sulfonate Four weight sections 1-ethoxy-2-propanol Spin spreading of the resist solution which consists of the 600 weight sections was carried out by 2,000rpm at the silicon substrate, and it prebaked for 1 minute at 85 degrees C on the hot plate. Thickness was 0.4 micrometers. After drawing with a KrF excimer laser or an electron ray with an acceleration voltage of 30kV, for [PEB] 2 minutes was performed at 85 degrees C. In the water solution of 2.4% of tetramethylammonium hydroxide (TMAH), development was performed for 1 minute and the rinse was carried out for 30 seconds with water.

[0054] This resist ingredient showed the property of a positive type, and D0 sensibility was 3.5microC/cm². Eth sensibility when it replaces with an electron ray and the KrF excimer laser light (wavelength of 248nm) which is far ultraviolet rays estimates was 3.2 mJ/cm². The base resin used here showed the dissolution rate of 30 nm/s to the developer. In this resist ingredient, the unexposed part had the dissolution rate of about 1.7 nm/s, and the exposure section had the dissolution rate of 45 nm/s after PEB.

[0055] In KrF excimer laser exposure, 0.25-micrometer Rhine and the tooth-space pattern, and the hole pattern resolved, and the pattern which has a perpendicular side attachment wall to a substrate has been formed. Moreover, 0.1 micrometers resolved in electron beam lithography.

[0056] [Examples 2-8] The acid generator was replaced with the base resin list in an example 1 as it was at Table 1, and the same approach as an example 1 estimated the KrF resist property. Sensibility and definition are shown in Table 1.

[0057] [Example 9]

Base resin (synthetic example 2) 80 weight sections Lysis inhibition agent (1, 3-(2-hydroxy carbonylethyl)-1, 3-TE truck methyl disiloxane) 16 weight sections Tori (p-t-butoxy phenyl) trifluoromethane sulfonate Four weight sections 2-ethoxy propanol Spin spreading of the resist solution which consists of the 700 weight sections was carried out by 2,000rpm at the silicon substrate, and it prebaked for 1 minute at 85 degrees C on the hot plate. Thickness was 0.4 micrometers. After drawing with a KrF excimer laser or an electron ray with an acceleration

voltage of 30kV, for [PEB] 2 minutes was performed at 85 degrees C. In the water solution of 2.4% of tetramethylammonium hydroxide (TMAH), development was performed for 1 minute and the rinse was carried out for 30 seconds with water.

[0058] This resist ingredient showed the property of a positive type, and D0 sensibility was 4microC/cm2. D0 sensibility when it replaces with an electron ray and the KrF excimer laser light (wavelength of 248nm) which is far ultraviolet rays estimates was 5.0 mJ/cm2.

[0059] In KrF excimer laser exposure, 0.25-micrometer Rhine and the tooth-space pattern, and the hole pattern resolved, and the pattern with a perpendicular side attachment wall has been formed. Moreover, 0.1 micrometers resolved in electron beam lithography. A result is shown in Table 2.

[0060] [Examples 10-12] The base resin in an example 9 was replaced with as shown in Table 2, and the same approach as an example 2 estimated the KrF resist property. Sensibility and definition are shown in Table 2.

[0061]

[Table 1]

実施例	ベース樹脂	酸発生剤	Eth 感度 (mJ/cm ²)	解像線幅 (μm)
1	合成例2のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	3.2	0.25
2	"	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	7.0	0.25
3	合成例3のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	3.5	0.25
4	"	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	7.0	0.25
5	合成例4のポリマー	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	4.2	0.25
6	"	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	9.0	0.25
7	合成例5のポリマー	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	12.0	0.25
8	"	p-tert-ブトキシフェニルジフェニルト ルエンスルフォネート	25.0	0.25

[0062]

[Table 2]

実施例	ベース樹脂	酸発生剤	Eth 感度 (mJ/cm ²)	解像線幅 (μm)
9	合成例2のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	5.0	0.25
10	合成例3のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	5.5	0.25
11	合成例4のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	6.5	0.25
12	合成例5のポリマー	p-tert-ブトキシフェニルジフェニルト リフルオロメタンスルフォネート	15.0	0.25

[0063] [Example 13] A resist solution is adjusted by the same presentation as an example 1,

and OFPR800 (Tokyo adaptation shrine make) is applied to a silicon wafer as a lower layer resist at the thickness of 2 micrometers, and it heated for 1 hour and was made to harden at 200 degrees C. The resist ingredient of an example 1 was applied and prebaked by about 0.4-micrometer thickness by the same approach as an example 1 on this lower layer resist. Negatives were exposed and developed with the electron ray or the KrF excimer laser like the example 1, and the pattern was formed on the lower layer resist.

[0064] Then, it etched by making oxygen gas into an etchant gas with parallel monotonous mold sputter etching equipment. The resist of a presentation of an example 1 was 3 or less nm/min to the etch rates of a lower layer resist being 150 nm/min. By etching for 15 minutes, the lower layer resist of the part which is not covered with a resist disappeared completely, and has formed the two-layer resist pattern with a thickness of 2 micrometers or more. This etching condition is shown below.

Quantity of gas flow: 50SCCM, gas pressure:1.3Pa rf power:50W, dc bias:450V[0065]

[Examples 14-24] The same pattern was able to be formed, when it replaced with the resist of an example 1 and the resist ingredient of examples 2-8 was etched as a two-layer resist on the same conditions as an example 13.

[Translation done.]